Can soil gas profiles be used to assess microbial CH_4 oxidation in landfill covers?

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Abstract

A method is proposed to estimate CH_4 oxidation efficiency in landfill covers, biowindows or biofilters from soil gas profile data. The approach assumes that the shift in the ratio of CO_2 to CH_4 in the gas profile, compared to the ratio in the raw landfill gas, is a result of the oxidation process and thus allows the calculation of the cumulative share of CH_4 oxidized up to a particular depth. The approach was validated using mass balance data from two independent laboratory column experiments. Values corresponded well over a wide range of oxidation efficiencies from less than 10% to nearly total oxidation. An incubation experiment on 40 samples from the cover soil of an old landfill showed that the share of CO_2 from respiration falls below 10 % of the total CO_2 production when the methane oxidation capacity is 3.8 µg CH_4 g_{dw}^{-1} h^{-1} or higher, a rate that is often exceeded in landfill covers and biofilters, according to a recent review paper. The method is mainly suitable in settings where the CO_2 concentrations are not significantly influenced by processes such as respiration or where CH_4 loadings and oxidation rates are high enough so that CO_2 generated from CH_4 oxidation outweighs other sources of CO_2. The latter can be expected for most biofilters, biowindows and biocovers on landfills. This simple method constitutes an inexpensive complementary tool for studies that require a reasonable estimation of the CH_4 oxidation efficiency values in passive methane oxidation systems, such as landfill biocovers and biowindows.

Key words: passive methane oxidation / soil respiration / greenhouse gases

1. Introduction

The microbial oxidation of methane in cover soils, biofilters or biowindows is considered a potent option for the mitigation of fugitive and low calorific emissions from landfills, i.e. CH_4 fluxes that cannot be utilized for energy recovery because either the gas generation rate and/or the CH_4 content are too low. (e.g. Barlaz et al., 2004; Gebert and Gröngröft, 2006; Haubrichs and Widmann, 2006; Huber-Humer et al., 2008; Streese and Stegmann, 2003; Scheutz et al., 2004). As a consequence, the recent IPCC Working Group III assessment report (Bogner et al., 2007) has listed biocovers and biofilters as key mitigation technologies and practices to reduce greenhouse gas emissions from landfills.

As landfills are ranked as the second largest source of anthropogenic CH_4 emissions in Europe, making up for 28% of the total anthropogenic CH_4 emission at approximately 3.7 Gg/a for the EU-15 (EEA, 2009), the need to assess the efficiency of mitigation measures, such as the installation of a biocover or a biofilter, is paramount. This is particularly important in the context where gas extraction systems are one day turned off, while biogas production may continue for several decades. However, a reliable quantification of methane removal rates is possible only when the magnitude of the fluxes into and out of the cover are known - which rarely is the case (Cabral et al. 2009, 2010) - or estimated (e.g. Einola et al. 2008; 2009).

More recently, stable isotope probing has been applied to assess methane oxidation in landfill covers in situ (Chanton and Liptay, 2000; Börjesson et al., 2007; Chanton et al., 2008; Cabral et al. 2010). However, the high cost of the analyses and the extreme sensibility of calculated CH_4 oxidation efficiencies to infinitesimal variations in the magnitudes of the fractionation factor α_{ox} (e.g. Cabral et al. 2010) and the fractionation due to diffusive gas transport ($\alpha_{trans,\ diff}$; De Visscher et al., 2004) may difficult dissemination of the use of this technique.

In systems that are dominated by diffusion, such as terrestrial soils, gas profiles can be used to quantify gas fluxes and emissions to the atmosphere (Kim et al., 2007), provided that the effective diffusion coefficient of the material is known. The approach is limited by the fact that the effective diffusivity varies strongly with the share of air-filled pore volume (Moldrup et al., 2000), which in turn is directly affected by water content. Profiles of CH_4, CO_2 and O_2 in landfill covers or column studies have therefore only been used as a qualitative indicator of methane oxidation, and to localize the approximate depth of the methane oxidation horizon.

To date, the only guidance for oxidation in emission modelling is given in the IPCC Guidelines for National Greenhouse Gas Inventories (Pipatti and Svardal, 2006). For landfill gas models these guidelines recommend a 10% default value for CH_4 oxidation if a “suitable” cover is present. Higher values are only accepted when supported by research data relevant for the region, which are rare. The scarcity of data is partly due to the difficulty (and/or cost) in evaluating oxidation efficiencies. Given the economic relevance of considering proper oxidation percentages in passive methane mitigation systems, this paper explores the possibilities and limitations of quantifying the share of methane oxidized in landfill covers, biofilters or biowindows by means of the analysis of the shift in the ratio of CO_2 to CH_4 in the gas profile. The proposed methodology was validated by means of two independent laboratory column studies. The materials used were mineral soils and a mixture of soil and compost. The studies involved determination of gas profiles at several CH_4 loading rates.

The main limitation to the proposed approach are processes other than CH_4 oxidation that may affect this ratio, of which soil respiration is the main one. If the potential error introduced by these processes can, in specific cases, be either neglected or accounted for, the estimation of CH_4 oxidation can be accomplished using an inexpensive and technically simple methodology, thereby allowing replacement of the 10% default value for CH_4 oxidation in covers by more meaningful estimates. Further benefits would include the possibilities to: 1) easily assess

temporal and spatial dynamics of CH_4 oxidation in cover soils and thus to assess the influence of regulatory factors such as soil temperature and porosity or water content, and 2) estimate methane oxidation efficiency in landfills situated in developing countries using simple technological tools.

2. Materials and methods

2.1 Laboratory column studies and materials

For the first study, six columns were set up (**Fig. 1**) to test the five different types of soils provided by NV Afvalzorg, The Netherlands. Table 1 summarizes selected soil physical parameters of the five soils used in the first column experiment. Although all materials were sand-dominated, physical properties of the soils vary quite strongly, with bulk densities between 1.36 and 1.73 g cm^{-3} and, most importantly for gas transport, a water free pore volume between 14.6 and 25.9 vol.%. The TOC of the samples taken from the column study varied between 1.4 and 7.5 % (see also **Table 3**).

Fig. 1. Setup of the first laboratory column study using mineral soils.

Table 1.
Characteristics of the materials used in the first column study. ww = wet weight. dw = dry weight.

	Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
Texture(1)	sand	sand	sand	loamy sand	sandy loam	sandy loam
Compaction [% Proctor]	95	95	95	95	95	85
Weight soil [kg ww]	42.6	36.3	43.8	37.9	41.3	37.0
Bulk density [g dw cm^{-3}]	1.67	1.38	1.73	1.36	1.59	1.42
Solids volume [l]	14.6	11.8	14.8	11.7	13.4	12.0
Pore volume [l]	8.6	10.9	7.9	11.0	9.0	10.4
Pore volume [vol.%]	38.0	47.9	34.7	48.6	40.1	46.4
Water content [vol.%]	16.8	22.1	20.0	31.0	25.7	23.0
Gas volume [vol.%]	21.2	25.9	14.6	17.7	14.5	23.5

(1) Soil texture defined according to the World Reference Base (IUSS Working Group WRB, 2006).

96 In each column, an 80-cm high layer of soil material was compacted to approximately 95% of
97 the maximum Proctor density, after water contents had been adjusted to the equivalent of the
98 average of 6 and 30 kPa suction, i.e. field capacity. Column 6, containing the same material as
99 column 5, was compacted to only 85 % of the maximum Proctor density. This degree of
100 compaction was chosen to simulate the effect of circulation of heavy machinery.

101 In the bottom, a gas-distribution layer, consisting of 17 cm of coarse gravel (ϕ = 2 to 8 mm), was
102 installed. The top 10 cm served as air-filled headspace. The columns were continuously flushed
103 with moisturized synthetic landfill gas (40 vol.% CO_2, 60 vol.% CH_4) at flow rates varying from
104 1.65 to 4.99 l CH_4 m^{-2} h^{-1}. The headspace was permanently flushed with moisturized synthetical
105 air at an excess flow rate. Gas and air were moisturized by bubbling them through water.
106 Average temperature during the five months of the experiment was 19.3 °C. Inlet and outlet
107 fluxes were controlled with rotameters.

108 The second study employed a very similar experimental setup (see also Roncato, 2009). Two
109 types of materials that are commonly found at the Saint-Nicéphore landfill (Québec) were tested
110 and their characteristics are presented in Table 2. The first is a mixture made up of 5 volumes of
111 compost (before sieving) and 1 volume of coarse sand (D_{10} = 0.07mm; D_{85} = 0.8mm; coefficient
112 of uniformity, Cu = 4.3) (details given in Jugnia et al., 2008), The other material is a mixture of
113 equal proportions of 6.4 mm gravel and the sand-compost mixture. Two different heights of
114 samples were tested: 30 and 45 cm. The sand-compost was compacted to 85% of the Proctor
115 density, in order to simulate the conditions found in a field experiment using the same materials
116 (Cabral et al. 2009, 2010). The gravel-sand-compost mixture was compacted to 77% of the
117 Proctor, again to simulate actual field conditions.

Table 2.
Characteristics of the materials used in the second column study.

↓ Parameter Material →	Sand-compost (2 tests)	Sand-compost-gravel (4 tests)
Organic matter [%] (1)	18	6
Degree of saturation, Sr (initial)	59.8; 68.7	40.4; 62.6; 44.9; 41.0
Degree of sat., Sr (end; 0-10 cm)	75.9; 83.2	51.9; 60.7; 64.7; 53.9
Gs [specific gravity] (2)	2.24	2.74
n [total porosity]	0.63	0.48
Compaction [% Proctor] (3)	85	77
Bulk density [g dw cm^{-3}]	0.84	1.43

(1) ASTM D2974-00, Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils.
(2) CAN/BNQ 2501-070/2006, Soils - Determination of Relative Density of Solid Particles.
(3) CAN/BNQ 2501-250/2005, Soils - Determination of the Water-Density Relation - Standard Effort Compaction Test.

The columns were continuously flushed with a mixture of moisturized synthetic landfill gas (50 vol.% CO_2, 50 vol.% CH_4). The flow rates varied between 0.5 l CH_4 m^{-2} h^{-1} and 7.8 l CH_4 m^{-2} h^{-1}. The headspace was also continuously flushed with moisturized air. Flow rates were controlled by means of rotameters.

In the second study, a respiration test was performed after completion of each oxidation test. Instead of synthetic gas, N_2 was applied from the bottom, while air was introduced in the head space. Several ratios of N_2 flow to air flow were applied. For each ratio, the CO_2 concentration in the headspace was measured when it became stabilized. This CO_2 concentration is assumed to be the result of respiration, under conditions one finds in the field, i.e. concomitant to an upward flow of gas. The CO_2 concentration attributed to respiration is eventually subtracted from the total headspace CO_2 concentrations measured during the actual oxidation tests. The final results from these subtractions are the concentrations of CO_2 generated by CH_4 oxidation that are eventually used to calculate oxidation efficiencies using the proposed method.

Soil gas profiles (CH_4, CO_2, O_2, and N_2) were obtained by probing through butyl rubber stoppers. In the first study, they were inserted at nine depths: headspace, 5, 15, 25, 35, 45, 55, 65, and 75 cm below the soil surface. For the columns of the second study, samples were taken every 10 cm, starting from the bottom of the sample.

2.2 Batch assays

Batch assays were conducted to determine the potential CH_4 oxidation rate and the respiration rate of the soils tested in the first column study and of 40 mixed soil samples from the top 30 cm of the final cover of an old landfill in Northern Germany. The soil samples from the old landfill were classified as sandy loam (IUSS Working Group WRB, 2006). Their TOC content ranged between 0.5 and 4 % with a mean of 2.2 %.

Standard SCHOTT DURAN® laboratory bottles (100 ml) where filled in triplicate with 10 g of fresh soil. The soils from the first column test were investigated at the water content corresponding to the one in the respective column. The samples from the old landfill were sieved to 2 mm and adjusted to 60 % of the water holding capacity. Bottles where sealed with butyl rubber stoppers. For the CH_4 oxidation assay, the headspace composition was adjusted to 10 vol.% CH_4 by addition of an appropriate volume of pure CH_4. The bottles were then incubated at 20 °C in the dark. Concentrations of CH_4 and CO_2 in the headspace were monitored until all CH_4 was oxidized. Oxidation rates were calculated using the linear part of the CH_4 degradation curve as follows:

$$CH_{4ox\_pot} = \frac{dCH_4}{dt} \times \frac{Vol_{bottle} \times MM_{CH4} \times 10}{MVol \times dw_{soil} \times 24} \quad (1)$$

where
CH_{4ox_pot} = potential CH_4 oxidation capacity [µg g_{dw}^{-1} h^{-1}]
dCH_4/dt = slope of change in CH_4 concentration [vol.%] over time [d]
Vol_{bottle} = gas volume of bottle [ml]
MM_{CH4} = molar mass of CH_4 = 16 g/mol
MV = molar gas volume at the given temperature [l]
dw_{soil} = dry weight of soil [g].

Soil respiration was calculated from the linear increase in headspace CO_2 over a period of approximately 40 days according to the following equation:

$$CO_{2\,prod} = \frac{dCO_2}{dt} \times \frac{Vol_{bottle} \times MM_{CO2} \times 10}{MVol \times dw_{soil} \times 24} \quad (2)$$

where CO_{2prod} =CO_2 produced [µg g_{dw}^{-1} h^{-1}]
dCO_2/dt = slope of change in CO_2 concentration [vol.%] over time [d]
Vol_{bottle} = gas volume of bottle [ml]
MM_{CO2} = molar mass of CO_2 = 44 g/mol
MV = molar gas volume at the given temperature [l]
dw_{soil} = dry weight of soil [g].

2.3 Gas chromatography

The headspace composition of the columns in the first study as well as batch headspace concentrations were measured with a gas chromatograph (Shimadzu) equipped with a flame ionization detector (FID, GC 14 A subunit) and a thermal conductivity detector (TCD, GC 14 B subunit). Column gas profiles were measured with an Agilent JAS2 GC-FID/TCD equipped with two Inventory #AB002 capillary columns. For the second study, the concentrations of CH_4, CO_2, O_2 and N_2 were determined using a gas chromatograph (Micro GC 3000 A, Agilent) equipped with two columns: MolSieve 5 A (for O_2, N_2 and CH_4 measurements) and Plot Q (for CO_2 measurements).

2.4 Calculation of CH_4 oxidation efficiency based on CH_4 mass balances

CH_4 oxidation efficiencies were calculated from the fluxes into and out of the columns as follows:

$$Eff_{ox} = \frac{(flux_{in} - flux_{out})}{flux_{in}} \times 100 \quad (3)$$

where Eff_{ox} = % of CH_4 loading oxidized (oxidation efficiency)
$flux_{in}$ = CH_4 flux into the column (ml min^{-1}), calculated from the inlet flow rate and the known CH_4 concentration of the feed gas
$flux_{out}$ = CH_4 flux out of the column (ml min^{-1}), calculated from the outlet flow rate and the measured CH_4 concentration in the column headspace.

2.5 Calculation of CH_4 oxidation efficiency from soil gas profiles: proposed methodology

Landfill gas is typically composed of 55 to 60 vol.% CH_4 and 40 to 45 vol.% CO_2. As a consequence, the ratio of CO_2 to CH_4 varies from 0.67 to 0.82. Microbial oxidation of CH_4 in the landfill cover shifts this ratio to higher values, as CH_4 is consumed, producing CO_2. Provided that the main source of CO_2 is methane oxidation, this ratio allows for the quantification of the cumulative amount of CH_4 oxidized up to any particular depth within the profile, based on known concentrations of CO_2 and CH_4 in the raw landfill gas and in the pore gas, at the desired depth. The method is independent of the nature of the flux (diffusive or advective). It is also independent of the effect of dilution of the pore gas by the ingress of atmospheric air from the surface, since it considers that CH_4 and CO_2 are diluted to the same extent.

The following assumptions are made:

According to the nominal oxidation reaction ($CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$), 1 mol of CH_4 is converted to 1 mol of CO_2.

1. It is assumed that in a well established landfill cover or biofilter the size of the methanotrophic population is stable. Under these conditions there is no net transfer of carbon into the microbial biomass, i.e. assimilation of carbon will be in equilibrium with release of carbon due to cell decay.
2. CO_2 is produced by oxidation of CH_4 only. We assume this to be valid under conditions where the CO_2–CH_4 ratio is mainly controlled by CH_4 oxidation, i.e. respiration plays a minor role. This occurs in biofilters with high CH_4 loading and oxidation rates, as well as in common daily or temporary landfill covers. It may also occur in final covers, in cases where gas extraction systems are inefficient.
3. The gas phase CO_2 is in equilibrium with the liquid phase CO_2.
4. Precipitation of CO_2 is negligible, as is true for non-calcareous soils.
5. The system is under steady state.

Limitations stemming from the assumptions above are discussed in detail later in the text. As a result of assumptions 1 to 5, the volume of CH_4 oxidized equals the volume of CO_2 produced and the share of oxidized CH_4 at a certain depth *i*, x, can be derived from Eq. 4:

$$\frac{CO_{2\_LFG} + x}{CH_{4\_LFG} - x} = \frac{CO_{2\_i}}{CH_{4\_i}} \quad (4)$$

where x = share of oxidized CH_4 (vol.%)
CH_{4_LFG} = CH_4 concentration of the landfill gas (vol.%)
CO_{2_LFG} = CO_2 concentration of the landfill gas (vol.%)
CH_{4_i} = CH_4 concentration in depth i (vol.%)
CO_{2_i} = CO_2 concentration in depth i (vol.%).

According to Eq. 4, the concentration of CO_2 in the landfill gas plus the share of CO_2 produced by oxidation up to the depth *i*, divided by the concentration of CH_4 in the landfill gas minus the share of CH_4 oxidized up to this depth is equal to the ratio of concentrations between the two landfill gases at the same depth *i*.

By dividing the share of oxidized CH_4 up to depth *i* by the concentration of CH_4 in the landfill gas (CH_{4_LFG}), one obtains the cumulated percentage of CH_4 oxidized, i.e. the cumulated oxidation efficiency, Eff_{ox} (%):

$$Eff_{ox} = \frac{x}{CH_{4\_LFG}} \quad (5)$$

The proposed method hence utilizes the change in the carbon mass balance of the soil gas phase to quantify CH_4 oxidation. A very similar approach has been applied by Christophersen et al. (2001), who calculated bottom CH_4 fluxes at the base of a landfill cover and in situ CH_4 oxidation rates by using the ratio of CH_4 to CH_4 at the base of a landfill cover and comparing it to the ratio of the CH_4 flux to CO_2 flux leaving the cover.

3. Results and Discussion

3.1 Batch CH_4 potential oxidation and respiration

Potential CH_4 oxidation and respiration rates for the five soils investigated in the first column study varied between 0.24 and 0.54 µmol CH_4 g_{dw}^{-1} h^{-1} (3.8 and 8.6 µg CH_4 g_{dw}^{-1} h^{-1}, **Table 3**). The CO_2 evolution by respiration was between 1.0 and 1.8% of the observed CO_2 production from CH_4 oxidation. Except for the soil used in columns 5 and 6, the materials had not been previously exposed to landfill biogas. The values of the share of respiration presented in **Table 3** are thus conservative values. Given the apparent low proportion of CO_2 released by respiration, assumption 3 (see section 2.5) was assumed to be valid for the first column experiment. For the second column experiments, respiration values were determined as explained before and the associated results are discussed later in the paper.

Table 3.
Potential CH_4 oxidation and respiration rates for the column material determined in batch experiments.

Column no.	TOC [%]	CH_4 oxidation rate [µmol CH_4 g_{dw}^{-1} h^{-1}]			Respiration rate [µmol CO_2 g_{dw}^{-1} h^{-1}]			Share of respiration [%]
		Avg	Max	Min	Avg	Max	Min	Avg
1	2.0	0.24	0.26	0.20	0.0032	0.0034	0.0032	1.3
2	4.9	0.35	0.39	0.32	0.0041	0.0043	0.0041	1.2
3	3.0	0.23	0.23	0.23	0.0023	0.0023	0.0020	1.0
4	7.5	0.54	0.66	0.45	0.010	0.0102	0.0095	1.9
5, 6	1.4	0.33	0.36	0.30	0.006	0.0081	0.0013	1.8

For the 40 samples from the landfill cover soil, CH_4 oxidation rates varied between 0.0063 and 1.4 µmol CH_4 g_{dw}^{-1} h^{-1} (0.1 and 22 µg CH_4 g_{dw}^{-1} h^{-1}) and respiration rates ranged between 0.0045 and 0.32 µmol CO_2 g_{dw}^{-1} h^{-1} (0.2 and 14 µg CO_2 g_{dw}^{-1} h^{-1}). When the evolution of CO_2 from respiration is compared to the evolution of CO_2 from the combined processes of CH_4 oxidation and respiration (Fig. **2**), it becomes clear that contribution of respiration to the total share in CO_2 concentration is strongly dependent on the CH_4 oxidation rate. Indeed, as the methane oxidation rate increases, the share of respiratory CO_2 release decreases exponentially. For the given set

of samples, the relationship was best described by an asymptotic function according to which the share of respiratory CO_2 release falls below 10% of the total CO_2 release when the CH_4 oxidation rate exceeds 3.6 µg g_{dw}^{-1} h^{-1}. As reviewed by Scheutz et al. (2009), this rate has been exceeded in many studies investigating the methanotrophic potential of mineral landfill cover soils (e.g. Czepiel et al., 1996; Börjesson et al., 2004; Stein & Hettiaratchi, 2001; de Visscher et al., 2001; Park et al., 2009). In other words, the contribution of CO_2 from respiration to the total share of CO_2 can be considered negligible. As a consequence, for this particular set of results, the third assumptions necessary to use the proposed method is respected.

Fig. 2. Share of CO_2 evolution from respiration versus CH_4 oxidation rate. All data determined in batch experiments using 40 samples from a landfill cover soil. Symbols = average values; error bars = minimum and maximum.

3.3 Gas profiles and CH_4 oxidation: first column study

Fig. 3 shows the profiles of CH_4, CO_2, O_2 and N_2 associated with three conditions: high oxidation efficiency (column 1), intermediate (column 2) and low efficiency (column 4). Graph A (column 1) shows that the material was highly aerated, as indicated by the high concentrations of N_2 straight to the base of the column. A high ratio of CO_2 to CH_4 at the base of the soil material suggests that methane oxidation was already taking place in the gas distribution layer (for ratios of CO_2 to CH_4 see **Table 4**). In the situation depicted in graph B (**Fig. 3**), air penetrates into the column to a far lesser extent. As in graph A, the proportion of O_2 to is far less than in the air, indicating that O_2 is consumed. Finally, graph C shows a situation, where hardly any air penetrates into the column. Correspondingly, the nearly unchanged concentrations of CH_4 and CO_2 up to a depth of 5 cm indicate that no oxidation was taking place.

Fig. 3. Three exemplary soil gas profiles from the laboratory column study. A = column 1 (20.10.2007, inlet flux = 2.4 l m^{-2} h^{-1}), B = column 2 (03.12.2007; inlet flux = 5.0 l m^{-2} h^{-1}), C = Column 4 (21.11.2007, inlet flux = 3.6 l m^{-2} h^{-1}).

Table 4 gives the ratio of CO_2 to CH_4 calculated for each of the three cases shown in **Fig. 3**, while **Fig. 4** depicts their corresponding oxidation efficiencies calculated using Eq. 5. These results show that under conditions of insufficient air ingress (column 4), oxidation occurs only very near the surface. In column 2, oxidation occurred across the entire profile, with the top 15 cm contributing the most. In this example, the total Eff_{ox} is 58.6%, of which approximately 30% occur in the top 5 cm. In the case of column 1, nearly 100% CH_4 oxidation efficiency was already attained at a depth of 5 cm. Good aeration allowed for methanotrophic activity across the entire profile with the greatest relative share being effected within the top 35 cm. Figure 4 shows that the total oxidation efficiency calculated from the CO2-CH4 ratio, as can be derived from the value in depth 0 (= column headspace) compares extremely well to the oxidation efficiency calculated from mass balance (number given in box).

Table 4.
Ratios of CO_2 to CH_4 for the three exemplary gas profiles. Depth 0 = column headspace.

Depth [cm]	Column 1 20.10.2007	Column 2 03.12.2007	Column 4 21.11.2007
0	5002	3.07	0.82
5	1140	1.80	0.60
15	25	0.98	0.61
25	3.20	0.87	0.62
35	2.08	0.82	0.61
45	1.71	0.79	0.63
55	1.32	-	0.62
65	1.22	0.76	0.62
75	1.08	0.72	0.63

Fig. 4. Three examples of the CH_4 oxidation efficiency (Eff_{ox}) as calculated by Eq. 5 from the ratio of CO_2 to CH_4 in the laboratory column study. Depth 0 = headspace; Col. = column; Numbers in legend = date of sampling.

Fig. 5 presents a comparison between oxidation efficiencies obtained from mass balance calculations and using the proposed method (CO_2-CH_4 ratio) for the six column tests of the first study.

Fig. 5. Column study: Eff_{ox} (%) calculated by mass balance (Eq. 3) versus Eff_{ox} in the headspace calculated using the ratio of CO_2 to CH_4 (Eq. 5).

The oxidation efficiency calculated using the CO_2-CH_4 ratio in the column headspace compares very well to the oxidation efficiency calculated by mass balance (Eq. 3), with decreasing efficiencies corresponding to decreasing extents of air penetration (compare to the exemplary profiles of N_2 shown in Figure 3). Deviations from the ideal x=y scenario (f(x) = x) may result from various causes influencing the ratio of CO_2 to CH_4. For example, under-proportional release of CO_2 due to carbon assimilation during population growth causes an underestimation of oxidation. In cases of stress, respiration rates increase and more CO_2 is released, leading to higher CO_2-CH_4 ratios and thereby an overestimation of oxidation. Figure 5 shows only a few values of low CH_4 oxidation efficiency. Low efficiencies in the column study were always related to insufficient depth of air penetration. In these cases, CH_4 oxidation was restricted to the topmost centimetres of the column.

Fig. 6. Oxidation efficiencies obtained with the second study: (a) For high organic matter (O. M.) content (n = 13); (b) for low organic matter content (n = 13).

Fig. **6** presents a comparison between oxidation efficiencies obtained from mass balance calculations and the proposed method, with data from the second column study, where a material with high organic matter content (18%) and a material with lower organic matter content (6%) were used. It can be observed in Fig. **6**a that the proposed method overestimated oxidation efficiencies for the material containing high organic matter content (18%), although the overestimation was not as important in the higher end of the efficiency scale (i.e. Eff_{ox} in the vicinity of 75%) as in the lower end. Introduction of the correction for respiration resulted in slightly better estimates. In the particular case of this column study, this was attributed to several causes, among which, the following: (1) Measurements made in the beginning and the end of the tests showed that the degrees of saturation increased, particularly near the surface of the samples (Table 2). This increase is caused by the combined effects of oxidation, which also

produces water, and of water condensation (partly caused by humidification of the inlet air and the synthetic gas). In field conditions, water may evaporate or transpire out; however, in the laboratory, it keeps accumulating within the sample. The high humidity in one of the tests (Sr = 83.2%) may have led to a situation whereby anaerobic conditions resulted in shallower penetration of O_2, and some CO_2 production down below. The existence of anaerobic conditions and how it may have affected the CO_2:CH_4 ratio were not investigated in this column study.

The second cause of the overestimation of Eff_{ox} by the proposed method for one particular test (Fig. **6**a) may be related to the fact that methanotrophic activity was possibly not fully developed in the beginning of the test, leaving the available O_2 for respiration and hence, CO_2 production, by heterotrophic bacteria. Indeed, in this particular test, the initial Sr was relatively low (59.8%), which facilitated penetration of O_2. It must be noted that an investigation of the data base for this particular test showed that gas loadings did not affect the results, i.e. low efficiencies were found for low and high gas flow rates.

Fig. **6**b presents the comparison between oxidation efficiencies obtained with the mixture of sand, compost and gravel, whose organic matter is in the order of magnitude normally found in normal top soils (5%). It can be observed that before correction for respiration, the proposed method overestimates oxidation efficiencies, but not to the same extent as in the case of the material with high organic matter content (Fig. **6**a). Introduction of the correction for respiration led to an almost perfect alignment, i.e. $y = 0.94x + 3.84$; where y is the Eff_{ox} from the CO_2-CH_4 ratio x is the Eff_{ox} from mass balance calculations. This means that the proposed method adequately estimated the actual efficiencies. Unfortunately there are no data available for efficiencies below 50%.

3.4 Limitations of the proposed method

One of the limitations of the proposed method relates to the assumption of steady state gas flow conditions. As gas flow rates vary continuously with changing atmospheric pressure and precipitation, steady state is rarely obtained in the field. This can lead to an over - or underestimation of the efficiency, depending on the prevailing conditions. Consequently, occurrence of steady state may seem to be a farfetched assumption for actual landfill conditions. It can be hypothesized that reliable results (oxidation efficiencies) could be obtained if the proposed method were applied to gas profile data obtained during periods of stable weather conditions, and that uncertainties related to its use under transient conditions can be overcome by long-term field measurements covering all seasons and thus the range of possible climatic conditions. It has to be kept in mind that the method is meant to give an indication of the magnitude of the oxidation efficiency; not the exact value.

Another caveat is that the application of the method to field profiles may lead to an underestimation of the total oxidation efficiency if a relevant share of the oxidation occurs very near the surface (Cabral et al. 2009, 2010), while the top most samples of gas profiles are taken from below this upper crust. It is thus advisable to collect samples from as shallow depths as possible.

Finally, the proposed method is suitable only for application in settings in which the CO_2 concentrations are not significantly influenced by processes such as heterotrophic or autotrophic respiration. This implies that application is limited to materials and sites of low respiratory activity, or when the quantities of CO_2 generated from respiration are small compared to generation from CH_4 oxidation. Respiration becomes negligible to the calculation of efficiencies based on the ratio of CO_2 to CH_4 under conditions of high CH_4 fluxes and high CH_4 oxidation rates. This was backed by the results presented, which suggested that beyond a threshold activity of approximately 3.8 µg CH_4 g dw^{-1} h^{-1} , the CO_2 production due to soil respiration falls

below 10% of the total CO_2 concentration. High fluxes prevail in biofilters or biowindows, providing preferential pathways for landfill gas or sites where a significant share of the produced landfill gas escapes via the soil cover, as is the case for most landfills in developing countries. In these setups performance could thus be very well quantified by the ratio of CO_2 to CH_4 in the soil gas phase.

CO_2 fluxes from natural soils vary with soil type, vegetation, season and diurnal course in temperature and radiation. Maximum values in temperate climates can reach between 0.2 and 0.7 l CO_2 m^{-2} h^{-1} (e.g. Kleber, 1997; Fang and Moncrieff, 2001; Richter et al., 1991; own measurements on fallow land). If a 10 % error on the results of oxidation efficiency due to respiratory CO_2 is to be accepted, CH_4 fluxes to and oxidation in the cover must be greater than at least 7 l CH_4 m^{-2} h^{-1} (approximately 5 g CH_4 m^{-2} h^{-1}). This magnitude is clearly exceeded in biofilters where inlet fluxes of 37 – 371 l CH_4 m^{-2} h^{-1} and CH_4 oxidation rates of 30 - 120 l CH_4 m^{-2} h^{-1} have been reported in field applications (Streese and Stegmann, 2003; Gebert and Gröngröft, 2006; Haubrichs and Widmann, 2006; Powelson et al., 2006; Zeiss, 2006). This magnitude of CH_4 loading is also exceeded in many landfill covers, particularly when the cover is not constructed following the same standards enforced by law in developed nations, in the last 15 to 25 years.

4. Conclusions

The proposed method represents an inexpensive and technically simple methodology to estimate the CH_4 oxidation efficiency values in passive methane oxidation systems, such as landfill biocovers, biowindows and biofilters by means of soil gas probing. It allows for a quantitative assessment of the overall CH_4 oxidation efficiency of these systems as well as for the stratification of the oxidation efficiency across the depth profile and thus for a better

398 understanding of the dependency of the process on key environmental variables such as
399 temperature and moisture.

400 Comparison of CH_4 oxidation calculated from the soil gas carbon balance and mass balance in
401 two independent column experiments with mineral soils intended for use as landfill cover
402 material showed an excellent correlation of CH_4 oxidation efficiency data, indicating the
403 applicability of the method in settings where the carbon balance is dominated by CH_4 oxidation.
404 As literature data show, this is true for many landfill cover soils and even more so for biofilters or
405 biowindows that usually receive high CH_4 loading rates. The findings were further substantiated
406 by activity tests of 40 samples from the topsoil of a landfill cover, showing that the production of
407 CO_2 from the process of CH_4 oxidation increases exponentially with the CH_4 oxidation rate and
408 that at rates > 3.6 µg g_{dw}^{-1} h^{-1} the CO_2 production from soil respiration becomes negligible. Other
409 settings where the proposed simple method can be applied include: daily or interim landfill
410 mineral cover soils that are usually not -or only sparsely- vegetated; and permanent soil covers
411 placed over non-sealed municipal solid waste landfills typically found in low-income countries.

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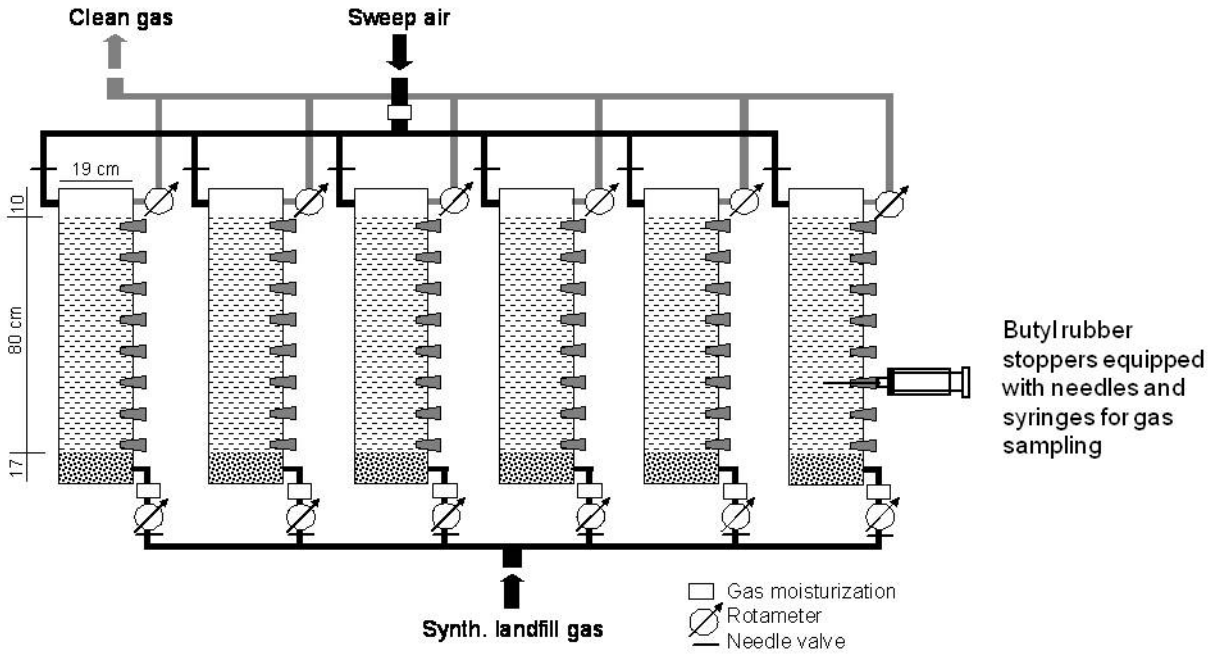

Fig. 1. Setup of the first laboratory column study using mineral soils.

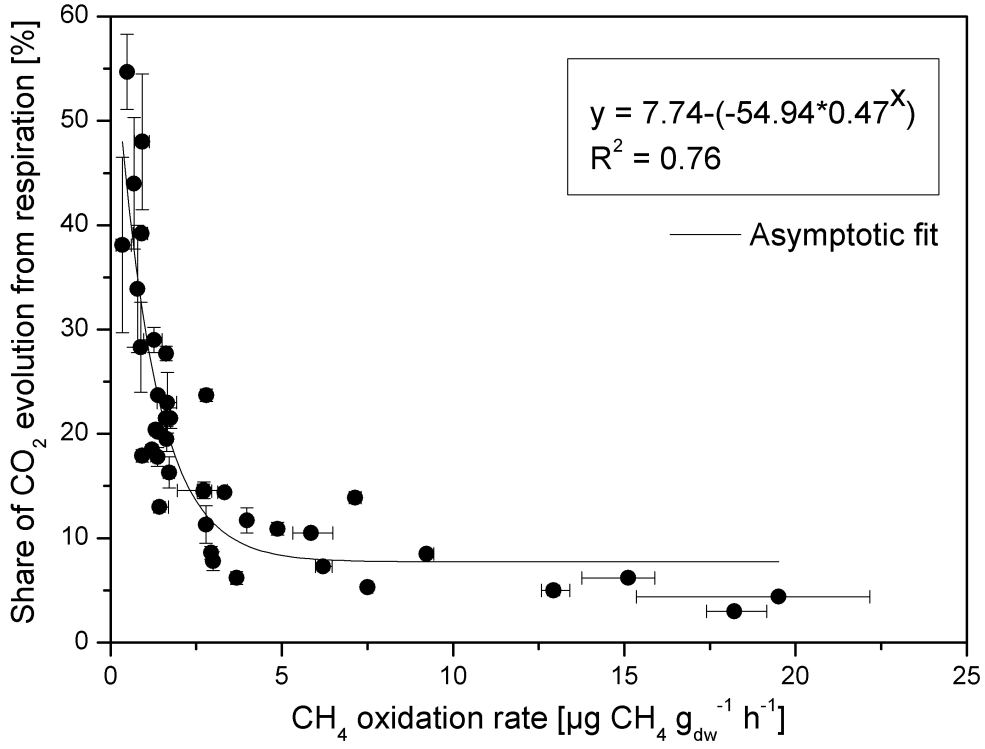

Fig. 2. Share of CO_2 evolution from respiration versus CH_4 oxidation rate. All data determined in batch experiments using 40 samples from a landfill cover soil. Symbols = average values; error bars = minimum and maximum.

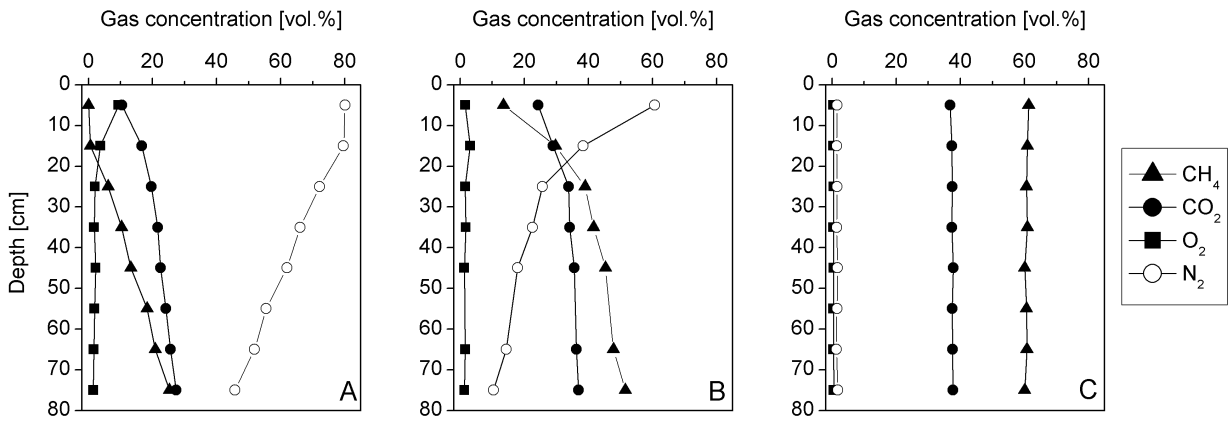

Fig. 3. Three exemplary soil gas profiles from the laboratory column study. A = column 1 (20.10.2007, inlet flux = 2.4 l m^{-2} h^{-1}), B = column 2 (03.12.2007; inlet flux = 5.0 l m^{-2} h^{-1}), C = Column 4 (21.11.2007, inlet flux = 3.6 l m^{-2} h^{-1}).

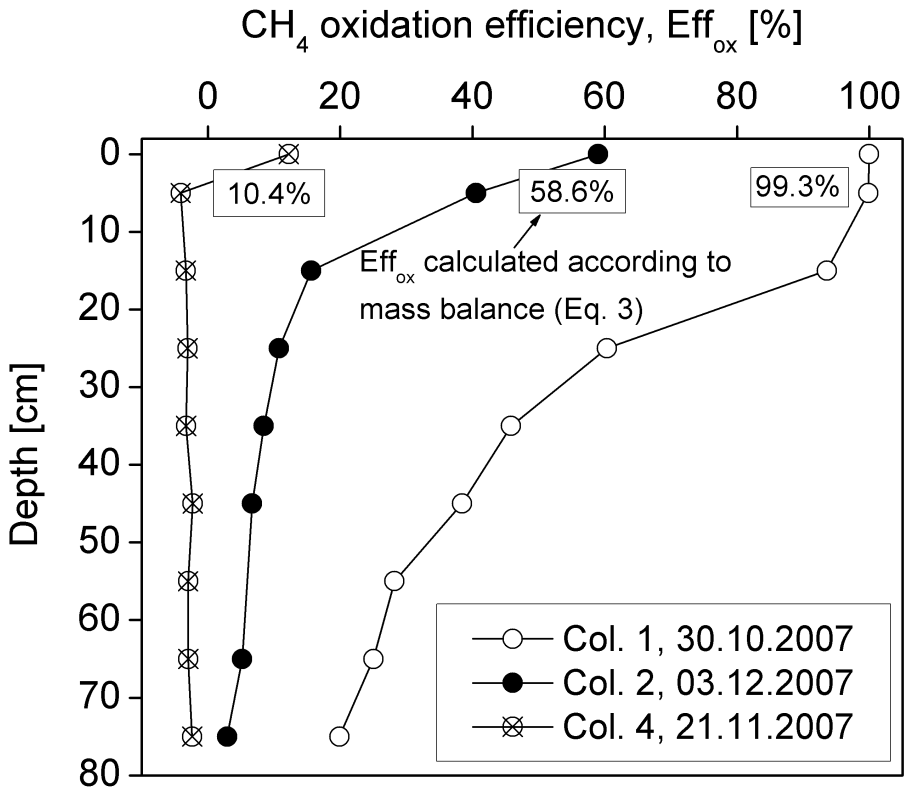

Fig. 4. Three examples of the CH_4 oxidation efficiency (Eff_{ox}) as calculated by Eq. 5 from the ratio of CO_2 to CH_4 in the laboratory column study. Depth 0 = headspace; Col. = column; Numbers in legend = date of sampling.

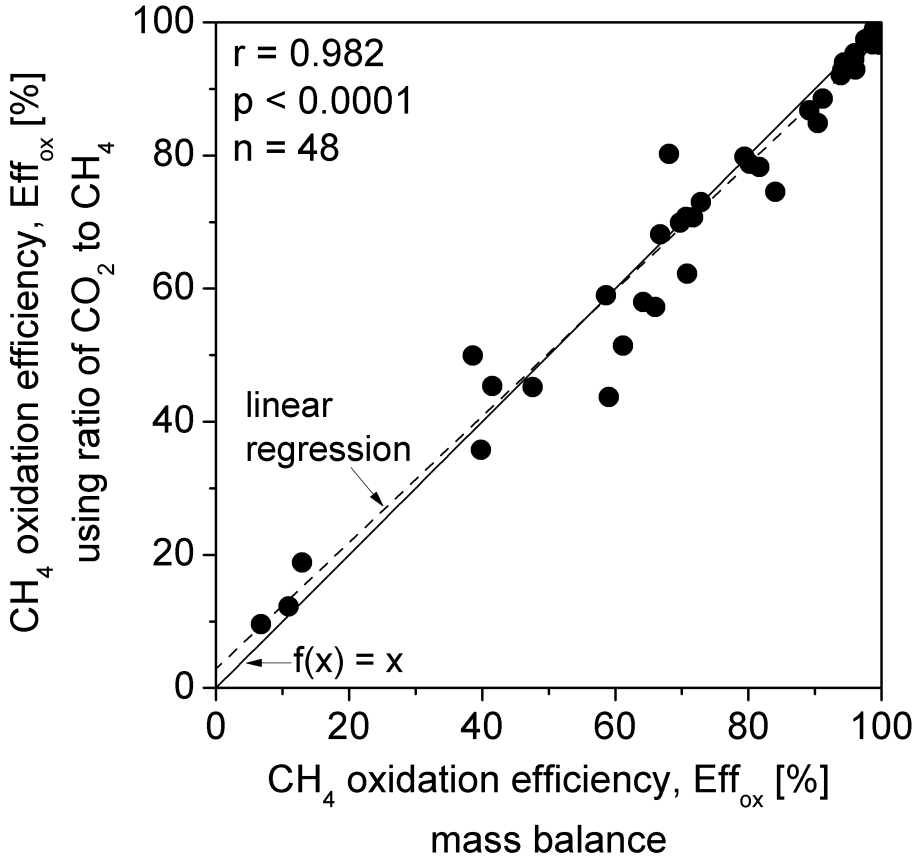

Fig. 5. Column study: Eff_{ox} (%) calculated by mass balance (Eq. 3) versus Eff_{ox} in the headspace calculated using the ratio of CO_2 to CH_4 (Eq. 5).

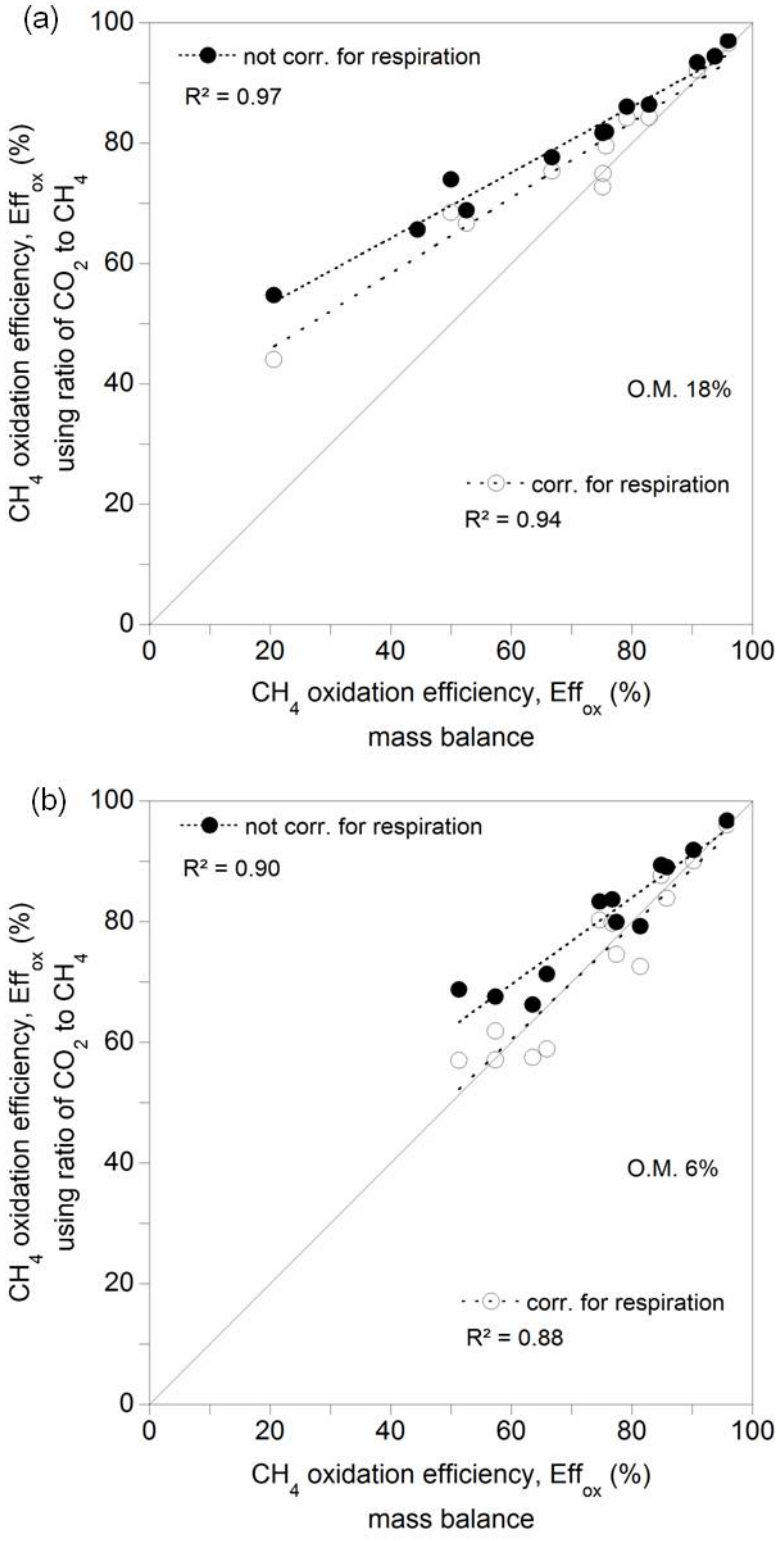

Fig. 6. Oxidation efficiencies obtained with the second study: (a) For high organic matter (O. M.) content (n = 13); (b) for low organic matter content (n = 13).